



# Synthesis and photocatalytic properties of tetragonal tungsten bronze type oxynitrides



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## ABSTRACT

Synthesis of a series of oxynitride  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  ( $x=0-1.5$ ) with a tetragonal tungsten bronze (TTB) structure was examined using moist- $\text{NH}_3$  and 5%  $\text{NH}_3\text{-N}_2$  as nitriding atmosphere. The samples with  $x=0-1$  were successfully obtained as phase pure TTB oxynitride whereas the  $x=1.5$  samples gave a mixture of TTB oxynitride,  $\text{Ta}_3\text{N}_5$ , and  $\text{LaTaO}_4$ . Absorption of TTB oxynitrides in visible region was enhanced as increasing the content of nitrogen. TTB oxynitrides exhibited both of  $\text{H}_2$  and  $\text{O}_2$  evolution under visible light in the presence of methanol and silver ions, respectively, as sacrificial reagents. Nitrogen poor surface in the samples synthesized under moist- $\text{NH}_3$  atmosphere was modified by annealing treatment using 5%  $\text{NH}_3$ , resulting in improvement of photocatalytic activity for  $\text{H}_2$  evolution. Evaluation using monochromatic light revealed that the apparent quantum efficiency of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  was higher than that of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$ .

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## 1. Introduction

Water splitting photocatalysts have attracted much attention as a potential method for the solar hydrogen production [1–5]. Various kinds of research, such as development of new photocatalysts [6–23], cocatalysts [17,24–30], synthesis method [31–38], and modification [39–43], are conducted to make progress in photocatalytic water splitting. Crystal structure is an important factor to classify photocatalyst materials. Perovskite structure is known as a promising one for photocatalysts in both of oxide and oxynitride [1–3,10,12,13,21,41].  $\text{SrTiO}_3\text{:Al}$  and  $\text{NaTaO}_3\text{:La}$ , representative perovskite-type oxide photocatalysts, can split water with very high quantum efficiency [44,45]. These photocatalysts function under only ultraviolet excitation whereas many perovskite-type photocatalysts with response to visible light are also reported.  $\text{SrTiO}_3\text{:Rh}$  is a well known visible light responsive oxide photocatalyst for  $\text{H}_2$  evolution [32,39,43,46]. In the oxynitride system, many perovskite-type  $\text{ABO}_2\text{N}$ ,  $\text{ABON}_2$ , and solid solutions are reported as visible light responsive photocatalysts and photoanodes [1–3,12,13,17,21,31,34,36,40,41]. Especially, Domen and co-workers have recently achieved overall water splitting under visible light using  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  modified with a metal oxyhydroxide layer [41]. In perovskite structure,  $\text{MX}_6$  octahe-

dra share corners with other octahedra to built characteristic framework. Tetragonal tungsten bronze (TTB) structure is common structure for materials with a general formula  $(\text{A}1)(\text{A}2)_2\text{B}_5\text{X}_{15}$  and is regarded as perovskite-related structure because it is also constituted of framework with corner-shared  $\text{MX}_6$  octahedra like as the perovskite structure (Fig. 1). Many TTB compounds, such as  $\text{K}_2\text{Ln}(\text{Nb,Ta})_5\text{O}_{15}$  ( $\text{Ln}$  = lanthanide),  $\text{KM}_2\text{Nb}_5\text{O}_{15}$ , and  $\text{tetr-BaTa}_2\text{O}_6$ , can drive overall water splitting and/or  $\text{CO}_2$  reduction in water under ultraviolet irradiation [1–3,11,37]. Nitride and oxynitride are attractive material group for visible-light-driven photocatalysts because N 2p orbital form valence band at shallower position than O 2p orbital [47]. Most of oxynitride photocatalysts are of perovskite compounds especially for  $d^0$ -based oxynitrides whereas oxynitrides with other structures such as  $\text{TaON}$ ,  $\text{GaN:ZnO}$ ,  $\text{C}_3\text{N}_4$ ,  $\text{Y}_2\text{Ta}_2\text{O}_5\text{N}$  and  $\text{MgTa}_2\text{O}_{6-x}\text{N}_y$  are also reported [1–3,6,19]. Lerch et al. have recently succeeded in synthesis of a TTB oxynitride  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  using a mixed gas of  $\text{NH}_3$  and  $\text{O}_2$  and revealed that  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  modified with a cocatalyst is active for  $\text{H}_2$  evolution from an aqueous methanol solution under visible light [22]. Here we report synthesis of nitrogen content-controlled  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  using either moist- $\text{NH}_3$  or  $\text{NH}_3\text{-N}_2$  atmosphere. Effects of annealing treatment on properties of surfaces and photocatalytic activities are also discussed.

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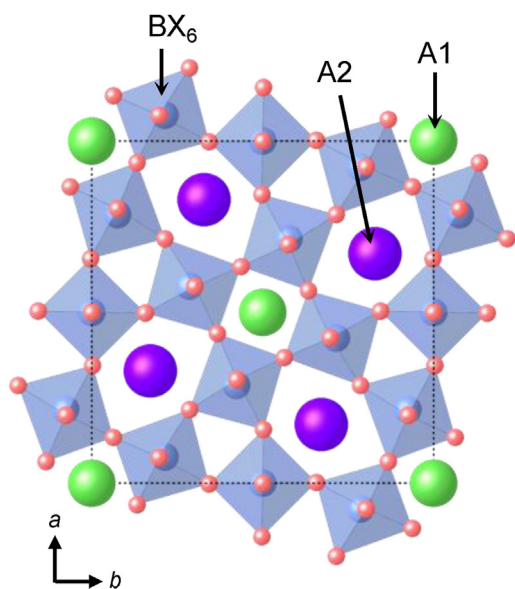


Fig. 1. General crystal structure of TTB compound (A1)(A2)<sub>2</sub>B<sub>5</sub>X<sub>15</sub>.

## 2. Experimental

### 2.1. Synthesis of Ba<sub>3-x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14-x</sub>N<sub>1+x</sub>

Powders of TTB-type oxynitrides Ba<sub>3-x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14-x</sub>N<sub>1+x</sub> were synthesized by nitridation of the corresponding amorphous oxide precursors. The precursors were obtained by a polymerizable complex method employing citric acid (CA, Wako Pure Chemical, 98%) and propylene glycol (PG, Kanto Chemical, 99.0%) as described elsewhere [21]. Barium carbonate (Kanto Chemical, 99.9%), lanthanum nitrate hexahydrate (Wako Pure Chemical, 99.9%), tantalum chloride (Furuuchi Chemical, 99.9%) were used as raw materials. PG, BaCO<sub>3</sub>, and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added to a methanol solution dissolving TaCl<sub>5</sub>. The solution was heated at 353 K with stirring until being a transparent solution and was heated at 423 K to promote condensation and esterification between CA and PG. The obtained viscous resin matter was subjected to sequential heating at 523, 623, and 723 K using a mantle heater to decompose organic matter. After pyrolysis, the residue carbon species was removed completely by heating at 823 K for 2 h using a box furnace. The oxide precursors thus obtained were amorphous. Nitridation of the oxide precursors was performed at 1073–1273 K for 10 h in a stream of pure NH<sub>3</sub>, 5% NH<sub>3</sub>-N<sub>2</sub>, or moist-NH<sub>3</sub> with a flow rate of 100 mL min<sup>-1</sup> using a tubular furnace. The moist-NH<sub>3</sub> flow was achieved by bubbling NH<sub>3</sub> gas through a saturated aqueous ammonia solution at 298 K.

### 2.2. Characterization of Ba<sub>3-x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14-x</sub>N<sub>1+x</sub>

Crystal phases of samples were identified by powder X-ray diffraction technique with Cu Kα radiation (XRD; Bruker AXS, D2 Phaser). Diffuse reflectance spectra in ultraviolet-visible region (UV-vis) were taken by an absorption spectrometer (Shimadzu, UV-3100) using an integrating sphere. Contents of N were analyzed by a combustion analyzer (Horiba, EMGA-620W). The composition at surface was determined by X-ray photoelectron spectroscopy (XPS; Kratos, ESCA-3200). The samples were observed by a scanning electron microscope (SEM; Hitachi, SU1510). Specific surface areas of the samples were determined by the BET method from N<sub>2</sub> adsorption isotherms (Micromeritics, ASAP-2010).

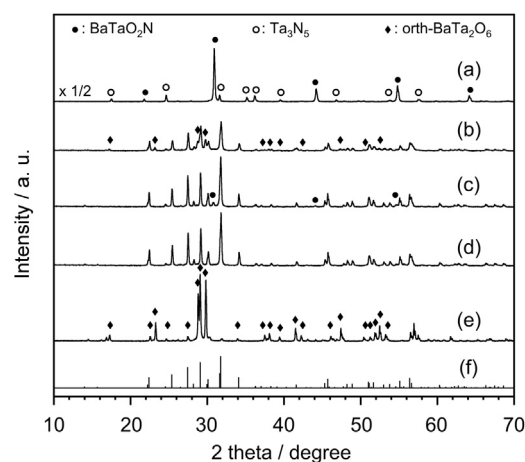


Fig. 2. XRD patterns of the samples obtained by nitridation of oxide precursors with Ba:Ta = (a–d) 3:5 and (e) 1:2 under various conditions; (a) 100% NH<sub>3</sub>, 1273 K, (b) 5% NH<sub>3</sub>, 1073 K, (c) 5% NH<sub>3</sub>, 1173 K, (d, e) moist-NH<sub>3</sub>, 1273 K. A simulated pattern of Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N is also presented as (f).

### 2.3. Evaluation of photocatalytic properties

Photocatalytic activities for H<sub>2</sub> and O<sub>2</sub> evolution in the presence of sacrificial reagents were measured using a gas-closed circulation system. The samples modified with 0.3 wt% of a Pt cocatalyst were used for H<sub>2</sub> evolution tests. Reactant solutions were 20 vol% methanol/water solution for H<sub>2</sub> evolution and 20 mM aqueous AgNO<sub>3</sub> solution with 0.1 g of La<sub>2</sub>O<sub>3</sub> powder as a pH buffer reagent for O<sub>2</sub> evolution. Photocatalyst (0.1 g) was dispersed in 150 mL of reactant solution in a reaction vessel with a top-window. Ten kPa of Ar was introduced into the system after deaeration. The suspended solution was irradiated with visible light (λ > 420 nm) using a 300 W Xe-arc lamp (Excelitas, Cermex PE300BF) with an optical cut-off filter. Monochromatic light from an illumination system (Asahi Spectra, MAX-303) was used for analysis of action spectra. Evolved gas was analyzed using an online gas chromatograph (Shimadzu, GC-14 B with MS-5A column, TCD detector, and Ar carrier). Apparent quantum efficiencies (η<sub>app</sub>) were determined by following equation,

$$\eta_{\text{app}}(\%) = (R_{\text{H}_2} \times 2) / \{I / ((1240/\lambda) \times 1.602 \times 10^{19} \times N_A)\} \times 100$$

where  $R_{\text{H}_2}$ ,  $I$ ,  $\lambda$  and  $N_A$  represent the rate of H<sub>2</sub> production in a unit of mol s<sup>-1</sup>, power of the monochromatic incident light in a unit of J s<sup>-1</sup> (W), wavelength of monochromatic light in a nm unit and the Avogadro constant, respectively.

## 3. Results and discussion

### 3.1. Synthesis condition of Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N

Nitridation of the oxide precursor with Ba:Ta = 3:5 was conducted under various conditions to find suitable nitriding condition for Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N (Fig. 2). The sample nitridized under pure NH<sub>3</sub> contained no TTB phases and was a mixture of perovskite-type BaTaO<sub>2</sub>N and Ta<sub>3</sub>N<sub>5</sub>. This result suggested that nitridation reaction proceeded too much for Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N under pure NH<sub>3</sub>. Then, nitridation using 5% NH<sub>3</sub>-N<sub>2</sub> was conducted to reduce the degree of nitridation. The TTB compound was formed as a major phase with small amount of BaTaO<sub>2</sub>N impurity in nitridation at 1173 K whereas a mixture of TTB compound and orth-BaTa<sub>2</sub>O<sub>6</sub> was obtained by nitridation at 1073 K. When nitridation was performed under a moist-NH<sub>3</sub> flow, single phase of TTB compound was obtained. The samples obtained by nitridation using 5% NH<sub>3</sub>-N<sub>2</sub> or moist-NH<sub>3</sub> were basically pale yellow although the sample nitridized at 1173 K

under 5%  $\text{NH}_3\text{-N}_2$  was reddish pale yellow due to the presence of trace amount of red  $\text{BaTaO}_2\text{N}$ . The results indicate that the TTB compound formed by the nitridation was TTB oxynitride  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  rather than tetr- $\text{BaTa}_2\text{O}_6$  that is one kind of the TTB oxides. In addition, when an oxide precursor with a ratio of Ba:Ta = 2.5:5 corresponding to the oxide phase  $\text{BaTa}_2\text{O}_6$  was treated at 1273 K under the moist- $\text{NH}_3$  flow, orth- $\text{BaTa}_2\text{O}_6$  of the low temperature polymorph of  $\text{BaTa}_2\text{O}_6$  was obtained as a main phase. Thus, being the ratio of Ba:Ta = 3:5 is essential to obtain pale yellow TTB compound by nitridation of Ba-Ta oxide. These results clearly indicate that the TTB compound formed by nitridation of precursor with Ba:Ta = 3:5 is not nitrogen-doped tetr- $\text{BaTa}_2\text{O}_6\text{-}_{3x}\text{N}_{2x}$  but  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$ . Indeed, the analyzed content of nitrogen was of 0.85 wt% in the single phase of TTB compound (moist- $\text{NH}_3$  sample) and was well consistent with the ideal value of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  (0.90 wt%). Thus, the present research reveals that synthesis of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  in high phase purity is possible by nitridation of the oxide precursor using 5%  $\text{NH}_3\text{-N}_2$  or moist  $\text{NH}_3$  flow beside  $\text{NH}_3\text{-O}_2$  flow reported previously [22].

### 3.2. Synthesis and characterization of $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$

We have previously reported that the increase in nitrogen content narrows band gaps of perovskite-type oxynitrides [21]. Substitution of  $\text{La}^{3+}$  for  $\text{Ba}^{2+}$  is possible strategy to increase the nitrogen content of TTB-type oxynitride according to formula  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$ . Fig. 3A shows XRD patterns of the samples obtained by nitridation of oxide precursors with Ba:La:Ta = 3- $x$ : $x$ :5 under the moist- $\text{NH}_3$  flow at 1273 K. The samples with  $x=0.5$  and 1.0 were obtained as a single phase of the TTB compound as well as  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  ( $x=0$ ) while the  $x=1.5$  sample was a mixture of TTB compound,  $\text{Ta}_3\text{N}_5$ , and  $\text{LaTaO}_4$ . Thus, the phase pure TTB oxynitride was obtained in cases with  $x \leq 1$ . This limit is owing to characteristics of the TTB structure. Two kinds of A-sites, that are 12-fold coordination site for A1 and 15-fold one for A2, exist in the TTB structure ( $(\text{A}1)(\text{A}2)_2\text{B}_5\text{X}_{15}$ ) as shown in Fig. 1. Although there are many TTB compounds in  $\text{K}_2\text{LnTa}_5\text{O}_{15}$ ,  $\text{KAE}_2\text{Ta}_5\text{O}_{15}$  ( $\text{AE} = \text{Sr}$  and  $\text{Ba}$ ), and  $\text{NaAE}_2\text{Ta}_5\text{O}_{15}$  systems, TTB compounds possessing smaller A-site cations than  $\text{Sr}^{2+}$  exceeding 1/3 of total A-sites, such as  $\text{Na}_2\text{LnTa}_5\text{O}_{15}$ ,  $\text{KCa}_2\text{Ta}_5\text{O}_{15}$  and  $\text{NaCaSrTa}_5\text{O}_{15}$ , have never been reported. It is because that only large cations such as  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{K}^+$  can occupy the A2-sites. According to this rule, A2-sites should be occupied by  $\text{Ba}^{2+}$  in the case of  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$ , meaning that the limit of lanthanum substitution is  $x=1$ . The contents of nitrogen in the samples increased with the La-substitution and were in good agreement with ideal values as shown in Table 1.

The synthesis of  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  was attempted using 5%  $\text{NH}_3\text{-N}_2$  (Fig. 3B). Phase pure TTB compounds were obtained for  $x=0.5$  and 1.0 as well as synthesis using moist- $\text{NH}_3$  although

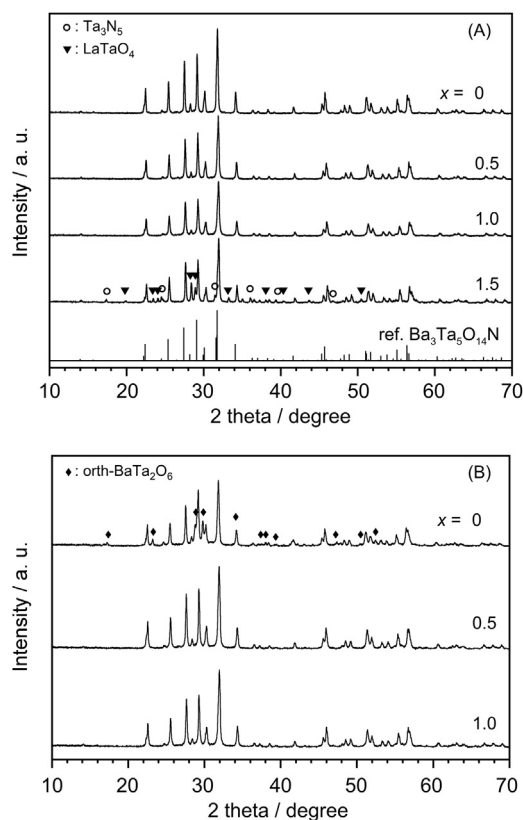


Fig. 3. XRD patterns of  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  obtained by nitridation using (A) moist- $\text{NH}_3$  at 1273 K for 10 h and (B) 5%  $\text{NH}_3$  at 1073 K for 10 h.

$\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  was not obtained as a single phase as described above. Thus, the window of synthesis conditions especially of nitriding atmosphere is expanded by the La-substitution. The increase in the target content of nitrogen by La-substitution would improve easiness in the synthesis of TTB-type oxynitride. The sharpness, intensity, and position of diffraction peaks were almost the same between samples synthesized in moist- $\text{NH}_3$  and 5%  $\text{NH}_3$  (Fig. S1). Moreover, no remarkable differences in contents of nitrogen were seen between samples synthesized under moist- $\text{NH}_3$  and 5%  $\text{NH}_3$ . Thus, both samples were identical with respect to bulk properties.

Fig. 4 shows UV-vis spectra of the samples obtained as phase pure TTB compounds. An absorption edge of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}$  remarkably shifted in comparison with that of tetr- $\text{BaTa}_2\text{O}_6$  which is an A-site deficient TTB oxide. The band gap of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}$  is estimated to be 2.8 eV, which consists with the value in the previous report [22]. The

Table 1  
Photocatalytic activity of  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  under visible light.

x	Synthesis condition	N content <sup>a</sup> / wt%	N/Ta ratio <sup>b</sup>	Activity / $\mu\text{mol h}^{-1}$	
				$\text{H}_2$ <sup>c</sup>	$\text{O}_2$ <sup>d</sup>
0	Moist- $\text{NH}_3$	0.85/0.90	0.07	0.8	0.3
	Annealed/moist- $\text{NH}_3$	1.00/0.90	0.21	1.9	0.9
0.5	Moist- $\text{NH}_3$	1.17/1.35	ND <sup>e</sup>	0.8	0.4
	5% $\text{NH}_3\text{-N}_2$	1.18/1.35	ND <sup>e</sup>	1.5	0.3
1	Moist- $\text{NH}_3$	1.58/1.80	0.14	0.7	0.3
	Annealed/moist- $\text{NH}_3$	2.05/1.80	0.33	2.6	0.3
	5% $\text{NH}_3\text{-N}_2$	1.63/1.80	0.22	3.7	0.3

<sup>a</sup> Measured value/identical value.

<sup>b</sup> Determined from XPS analysis.

<sup>c</sup> Measured for Pt (0.3 wt%)-loaded sample.

<sup>d</sup> Measured without cocatalyst.

<sup>e</sup> Not determined.

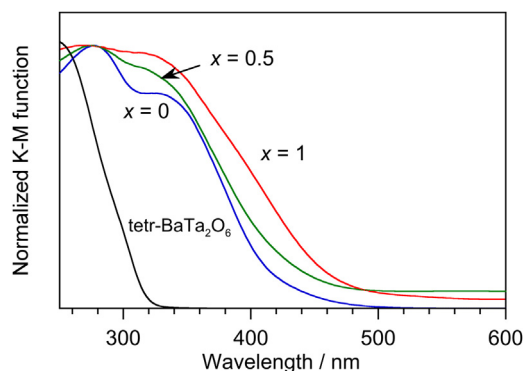


Fig. 4. UV-vis spectra of  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$ .

remarkable red shift is due to contribution of N 2p orbital to band structure. In the absorption spectrum of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}$ , an absorption band appears in UV region. This absorption band is similar to band gap absorption in tetr- $\text{BaTa}_2\text{O}_6$  corresponding to electron transition from O 2p to Ta 5d. This result suggests that N 2p orbitals form electron donor levels rather than valence band. It is reasonable in consideration of small contribution of N 2p owing to low concentration of N in  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$ . The absorption in visible region became intense as increasing La-substitution and the absorption band owing to transition from O 2p to Ta 5d became unobvious. Thus, enhancement of visible light absorption is achieved by increasing the content of nitrogen with La-substitution.

### 3.3. Photocatalytic activity of $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$

Photocatalytic activities of  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  are summarized in Table 1. All samples exhibited photocatalytic  $\text{H}_2$  and  $\text{O}_2$  evolution in the presence of sacrificial reagents under visible light. The samples synthesized under moist- $\text{NH}_3$  evolved  $\text{H}_2$  in rates of 0.7–0.8  $\mu\text{mol/h}$  irrespective of the composition. The samples synthesized in 5%  $\text{NH}_3$  showed higher activity for  $\text{H}_2$  evolution than ones synthesized moist- $\text{NH}_3$ . The activity of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  for  $\text{H}_2$  evolution was higher than that of  $\text{Ba}_{2.5}\text{La}_{0.5}\text{Ta}_5\text{O}_{13.5}\text{N}_{1.5}$ . As mentioned above, there are no differences in crystallinity and contents of nitrogen between samples synthesized in moist- $\text{NH}_3$  and 5%  $\text{NH}_3$ . Moreover, there are no differences in morphological properties between the moist- $\text{NH}_3$  and 5%  $\text{NH}_3$  samples of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$ , that is, both samples are composed of large secondary particles in which fine featureless primary particles are aggregated and sintered as shown in Fig. S2. However, XPS analysis of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  revealed that the ratio of nitrogen at the surface changed by the nitriding atmosphere although no change in chemical states of Ta and N (Fig. 5a and c). The ratio of N/Ta was 0.14 in the moist- $\text{NH}_3$  sample while that was increased to 0.22 in the 5%  $\text{NH}_3$  sample (Table 1). Partial oxidation of surface by water vapor competitively occurs in nitridation process using moist- $\text{NH}_3$  [48], resulting in the poor nitrogen surface. These results suggest that the low activities of the moist- $\text{NH}_3$  samples are due to the nitrogen poor surfaces (Fig. 6). Annealing treatment at 1073 K for 10 h using 5%  $\text{NH}_3$  was performed for the moist- $\text{NH}_3$  samples of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  and  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  to modify the surfaces. No changes in chemical states of Ta and N were observed again in XPS analysis (Fig. 5a and b). However, the ratio of N/Ta in XPS analysis greatly increased from 0.14 to 0.33 by the annealing treatment of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  whereas the slight increase in the bulk content of nitrogen and no changes in XRD patterns were observed as shown in Table 1 and Fig. S3. The similar effects of the annealing treatment were also observed for  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  without morphological changes (Fig. S4). Thus, annealing treatment using 5%  $\text{NH}_3$  at 1073 K mainly affected the

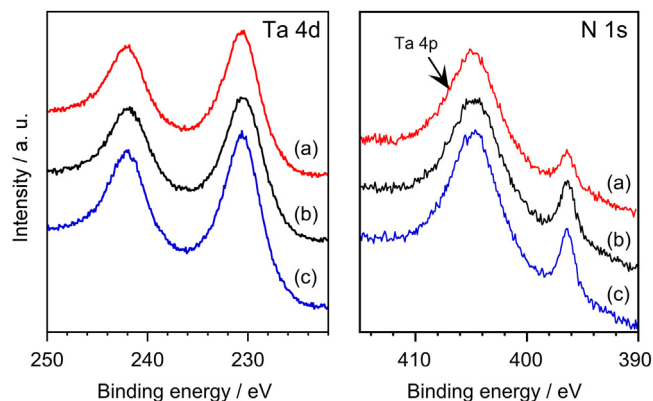


Fig. 5. XPS in Ta 4d and N 1s regions of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$ ; (a) synthesized in moist- $\text{NH}_3$ , (b) annealed (a), and (c) synthesized in 5%  $\text{NH}_3$ .

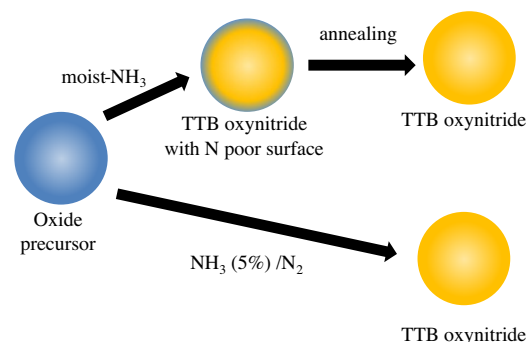


Fig. 6. Changes in surface status by synthesis methods.

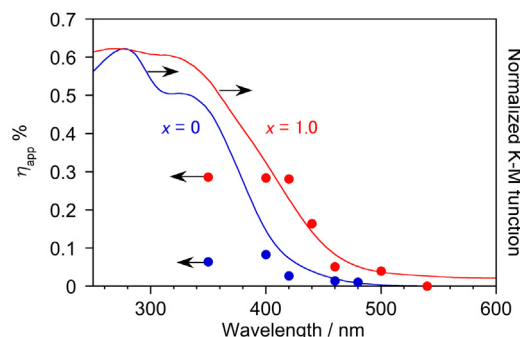


Fig. 7. Action spectra of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  and  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  ( $x = 1$ ) for  $\text{H}_2$  evolution together with their UV-vis spectra.

surface properties. The activities of both samples for  $\text{H}_2$  evolution were improved by the annealing treatment. However, for  $\text{O}_2$  evolution, annealing treatment improved the activity of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  but did not affect for  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$ . The specific surface area of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  ( $6.5 \text{ m}^2 \text{ g}^{-1}$ ) was larger than that of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  ( $2.5 \text{ m}^2 \text{ g}^{-1}$ ), indicating  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  composed of smaller particles. It has been reported that small particles are not effective for photocatalytic  $\text{O}_2$  evolution of a 4-electron reaction [49]. It is assumed that  $\text{O}_2$  evolution is tough for  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  composed of small particles, resulting in a poor effect of the annealing treatment.

Action spectra of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  and  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  for  $\text{H}_2$  evolution are shown in Fig. 7 together with their UV-vis spectra. The annealed moist- $\text{NH}_3$  sample and the 5%  $\text{NH}_3$  sample were used for  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  and  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$ , respectively, in measurement of action spectra.  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  showed higher  $\eta_{\text{app}}$  than  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  in entire range; for example 0.3% and 0.1% at 400 nm. The larger mobility of photogenerated holes, which is



caused by the larger contribution of N 2p orbital owing to higher content of nitrogen in Ba<sub>2</sub>LaTa<sub>5</sub>O<sub>13</sub>N<sub>2</sub>, would result in higher  $\eta_{\text{app}}$ . In addition, an onset wavelength in the action spectrum of Ba<sub>2</sub>LaTa<sub>5</sub>O<sub>13</sub>N<sub>2</sub> was obviously shifted to longer wavelength side like as UV–vis spectrum. However,  $\eta_{\text{app}}$  at 350 nm was almost the same as that at 400 nm although larger numbers of photogenerated e<sup>−</sup>/h<sup>+</sup> pairs were expected from stronger absorption at 350 nm. The factors other than surface reactivity and photogeneration of e<sup>−</sup>/h<sup>+</sup> would limit  $\eta_{\text{app}}$ . The interior and/or inter-particle mobility of e<sup>−</sup>/h<sup>+</sup> would be still low although the mobility of holes is improved by increasing the nitrogen content. Such low mobility of photogenerated carriers spoil the advantage of larger number of photogenerated e<sup>−</sup>/h<sup>+</sup>, resulting in the relatively low apparent quantum efficiencies at 350 nm. As described above, it has found that La-substitution improves photocatalytic activity of TTB oxynitride with points of view not only from the increase in the ability of visible light absorption but also from enhancement of efficiency.

#### 4. Conclusions

TTB oxynitrides Ba<sub>3−x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14−x</sub>N<sub>1+x</sub> ( $x=0, 0.5$ , and  $1$ ) have been successfully synthesized using moist-NH<sub>3</sub> as a nitriding atmosphere whereas TTB oxynitride with  $x > 1.5$  has not been obtained. It is concluded that the limit of La-substitution is  $x=1$  because small cation La<sup>3+</sup> cannot occupy the 15-fold site. TTB oxynitrides with  $x=0.5$  and  $1$  can also be obtained in pure phase using 5% NH<sub>3</sub> as a nitriding atmosphere. TTB oxynitrides exhibit photocatalytic activities for sacrificial H<sub>2</sub> and O<sub>2</sub> evolution under visible light. The samples synthesized under moist-NH<sub>3</sub> show lower activities than the samples synthesized or annealed in 5% NH<sub>3</sub> atmosphere. Low activities of the moist-NH<sub>3</sub> sample are due to the nitrogen poor surfaces. Thus, it has been found that the annealing treatment using diluted NH<sub>3</sub> gas is one of the ways to improve the photocatalytic activity of oxynitrides. The increase in the content of nitrogen achieved by the La-substitution causes red-shifts of onset wavelengths in absorption and action spectra. It is presumed that the larger contribution of N 2p orbital also enhances photocatalytic efficiency of TTB oxynitrides due to the improvement of the mobility of photogenerated holes.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.01.057>.

#### References

- [1] F.E. Oserloh, *Chem. Mater.* 20 (2008) 35–54.
- [2] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* 38 (2009) 253–278.
- [3] X. Chen, S. Shen, L. Guo, S. Mao, *Chem. Rev.* 110 (2010) 6503–6570.
- [4] K. Maeda, K. Domen, *J. Phys. Chem. Lett.* 1 (2010) 2655–2661.
- [5] B.A. Pinaud, J.D. Benck, L.C. Seitz, A.J. Forman, Z. Chen, T.G. Deutsch, B.D. James, K.N. Baum, G.N. Baum, S. Ardo, H. Wang, E. Miller, T.F. Jaramillo, *Energy Environ. Sci.* 6 (2013) 1983–2002.
- [6] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* 8 (2009) 76–80.
- [7] M. Tabata, K. Maeda, T. Ishihara, T. Minegishi, T. Takata, K. Domen, *J. Phys. Chem. C* 114 (2010) 11215–11220.
- [8] Q. Jia, Y. Miseki, K. Saito, H. Kobayashi, A. Kudo, *Bull. Chem. Soc. Jpn.* 83 (2010) 1275–1281.
- [9] Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu, R.L. Withers, *Nat. Mater.* 9 (2010) 559–564.
- [10] J.S. Jang, P.H. Borse, J.S. Lee, K.T. Lim, C.R. Cho, E.D. Jeong, M.G. Ha, M.S. Won, H.G. Kim, *J. NanoScale Nanotechnol.* 10 (2010) 5008–5014.
- [11] Y. Miseki, A. Kudo, *ChemSusChem* 4 (2011) 245–251.
- [12] S. Chen, J. Yang, C. Ding, R. Li, S. Jin, D. Wang, H. Han, F. Zhang, C. Li, *J. Mater. Chem. A* 1 (2013) 5651–5659.
- [13] T. Hisatomi, C. Katayama, Y. Moriya, T. Minegishi, M. Katayama, H. Nishiyama, T. Yamada, K. Domen, *Energy Environ. Sci.* 6 (2013) 3595–3599.
- [14] P.P. Sahoo, P.A. Maggard, *Inorg. Chem.* 52 (2013) 4443–4450.
- [15] H. Kato, A. Takeda, M. Kobayashi, M. Kakihana, *Chem. Lett.* 42 (2013) 744–746.
- [16] H. Kato, A. Takeda, M. Kobayashi, M. Hara, M. Kakihana, *Catal. Sci. Technol.* 3 (2013) 3147–3154.
- [17] K. Maeda, K. Domen, *Bull. Chem. Soc. Jpn.* 89 (2013) 627–648.
- [18] L. Wang, B. Cao, W. Kang, M. Hybertsen, K. Maeda, K. Domen, P.G. Khalifah, *Inorg. Chem.* 52 (2013) 9192–9205.
- [19] S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Asai, Z. Li, S.S. Ma, F. Zhang, K. Domen, C. Li, *Angew. Chem. Int. Ed.* 54 (2015) 8498–8501.
- [20] H. Kato, T. Fujisawa, M. Kobayashi, M. Kakihana, *Chem. Lett.* 44 (2015) 973–975.
- [21] H. Kato, K. Ueda, M. Kobayashi, M. Kakihana, *J. Mater. Chem. A* 3 (2015) 11824–11829.
- [22] B. Anke, T. Bredow, J. Soldat, M. Wark, M. Lerch, *J. Solid State Chem.* 233 (2016) 282–288.
- [23] H. Fujito, H. Kunioku, D. Kato, H. Suzuki, M. Higashi, H. Kageyama, R. Abe, *J. Am. Chem. Soc.* 138 (2016) 2082–2085.
- [24] K. Domen, S. Naito, M. Soma, T. Onishi, K. Tamaru, *J. Chem. Soc. Chem. Commun.* (1980) 543–544.
- [25] K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue, K. Domen, *Angew. Chem. Int. Ed.* 45 (2006) 7806–7809.
- [26] K. Maeda, K. Teramura, N. Saito, Y. Inoue, K. Domen, *J. Catal.* 243 (2006) 303–308.
- [27] A. Iwase, H. Kato, A. Kudo, *Catal. Lett.* 108 (2006) 7–10.
- [28] J.J.H. Pijpers, M.T. Winkler, Y. Surendranath, T. Buonassisi, D.G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.* 108 (2011) 10056–10061.
- [29] J. Yang, D. Wang, H. Han, C. Li, *Acc. Chem. Res.* 46 (2013) 1900–1909.
- [30] T. Kanazawa, D. Lu, K. Maeda, *Chem. Lett.* 45 (2016) 967–969.
- [31] A.E. Maegli, T. Hisatomi, E.H. Otal, S. Yoon, S. Pokrant, M. Grätzel, A. Weidenkaff, *J. Mater. Chem.* 22 (2012) 17906–17913.
- [32] H. Kato, Y. Sasaki, N. Shirakura, A. Kudo, *J. Mater. Chem. A* 1 (2013) 12327–12333.
- [33] H. Kato, M. Kobayashi, M. Hara, M. Kakihana, *Catal. Sci. Technol.* 3 (2013) 1733–1738.
- [34] Y. Mizuno, H. Wagata, K. Yubuta, N. Zettsu, S. Oishi, K. Teshima, *CrystEngComm* 15 (2013) 8133–8138.
- [35] D. Noureddine, D.H. Anjum, K. Takanabe, *Phys. Chem. Chem. Phys.* 16 (2014) 10762–10769.
- [36] T. Hisatomi, C. Katayama, K. Teramura, T. Takata, Y. Moriya, T. Minegishi, M. Katayama, H. Nishiyama, T. Yamada, K. Domen, *ChemSusChem* 7 (2014) 2016–2021.
- [37] T. Takayama, A. Iwase, A. Kudo, *Bull. Chem. Soc. Jpn.* 88 (2015) 538–543.
- [38] C.S. Quintans, H. Kato, M. Kobayashi, H. Kaga, A. Iwase, A. Kudo, M. Kakihana, *J. Mater. Chem. A* 3 (2015) 14239–14244.
- [39] A. Iwase, Y.H. Ng, Y. Ishiguro, A. Kudo, R. Amal, *J. Am. Chem. Soc.* 133 (2011) 11054–11057.
- [40] M. Matsukawa, R. Ishikawa, T. Hisatomi, Y. Moriya, N. Shibata, J. Kubota, Y. Ikuhara, K. Domen, *Nano Lett.* 14 (2014) 1038–1041.
- [41] C. Pan, T. Takata, M. Nakabayashi, T. Matsumoto, N. Shibata, Y. Ikuhara, K. Domen, *Angew. Chem. Int. Ed.* 54 (2015) 295–2959.
- [42] T. Takata, C. Pan, M. Nakabayashi, N. Shibata, K. Domen, *J. Am. Chem. Soc.* 137 (2015) 9627–9634.
- [43] Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I.D. Sharp, A. Kudo, T. Yamada, K. Domen, *Nat. Mater.* 15 (2016) 611–615.
- [44] H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.* 125 (2003) 3082–3089.
- [45] Y. Ham, T. Hisatomi, Y. Goto, Y. Moriya, Y. Sakata, A. Yamakata, J. Kubota, K. Domen, *J. Mater. Chem. A* 4 (2016) 3027–3033.
- [46] R. Konta, T. Ishii, H. Kato, A. Kudo, *J. Phys. Chem. B* 108 (2004) 8992–8995.
- [47] K. Maeda, K. Domen, *J. Phys. Chem. C* 111 (2007) 7851–7861.
- [48] E. Orhan, F. Tessier, R. Marchand, *Solid State Sci.* 4 (2002) 1071–1076.
- [49] F. Amano, E. Ishinaga, A. Yamakata, *J. Phys. Chem. C* 117 (2013) 22584–22590.